

Best Available Copy

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



Application No.: 10/824,876
Filing Date: April 15, 2004
Applicant: Gregory P. Meisner et al.
Group Art Unit: 1754
Examiner: Wayne A. Langel
Title: IMIDE/AMIDE HYDROGEN STORAGE
MATERIALS AND METHODS
Attorney Docket: GP-302579 (8540R-000027/DVA)

DECLARATION OF PRIOR INVENTION IN THE UNITED STATES TO OVERCOME A CITED PUBLICATION PURSUANT TO 37 C.F.R. §1.131

PURPOSE OF DECLARATION

1. I am a co-inventor of the patent application identified above and inventor of the subject matter described and claimed therein, including of Claims 17-26, 28-34, and 36-51.

2. This declaration is being presented to establish conception and reduction to practice of the invention of the patent application identified above in the United States at a date prior to November 21, 2002.

FACTS & DOCUMENTARY EVIDENCE

3. Prior to November 21, 2002, having earlier conceived of the concept of a method of forming an imide hydrogen storage material by reacting a hydride and an amide, I submitted a record of invention to the legal department at General Motors Corporation. To establish the date of conception of the invention of the claims of this patent application, the attached record of invention document is submitted as Exhibit A. Exhibit A also contains portions of an internal presentation relating to and summarizing the record of invention, which was prepared and

presented before November 21, 2002. The redacted portions of Exhibit A either disclose dates that are all prior to November 21, 2002 or disclose personal confidential information. This document (hereinafter referred to as the "ROI") was: prepared prior to November 21, 2002; identifies me as a co-inventor; and discusses and illustrates our conceived invention.

4. Prior to November 21, 2002, our invention was reduced to practice and experiments were conducted to generate data detailed in Figures 1 and 2 of the above identified patent application and in the lab notebook pages describing experimental details regarding lithium imide systems (attached as Exhibit B). The detailed description of the above identified patent application (at Paragraphs 36-42) details how the data was generated to create Figures 1 and 2, respectively. To establish the date of reduction to practice of the subject matter as claimed in this patent application, Exhibit B contains laboratory test data illustrating reduction to practice prior to November 21, 2002. The redacted portions of Exhibit B are dates that are all prior to November 21, 2002.

DECLARATION

5. As the person signing below: I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE

Dated: 11/30/2006



Gregory F. Meisner

EXHIBIT A

37 C.F.R. §1.131 Declaration of Gregory P. Meisner
U.S.S.N. 10/824,876 entitled "Imide/Amide Hydrogen Storage Materials and Methods."

GP-302579

INVENTION FILE OPENED

CLASS: _____

POSTPONED: _____

GP-302579

HYDROGEN STORAGE MEDIUM

Grégory P. Meisner
Frederick E. Pinkerton
Martin S. Meyer
Michael P. Balogh
Matthew D. Kundrat

R & D

Kathy Marra

302 579 (8540R file 27)



Research & Development and Planning

Date: [REDACTED]

Subj: R&D and Planning Record of Invention File No. GP-30257⁹

To: Kathryn A. Marra
GM Corporation Legal Staff
300 Renaissance Center
M.C. 482-C23-B21
P.O. Box 300
Detroit, MI 48265-3000

Attached is the Record of Invention entitled "Hydrogen Storage Medium" in the name(s) of Gregory P. Meisner (430), Frederick E. Pinkerton (430), Martin S. Meyer (430), Michael P. Balogh (460), and Matthew D. Kundrat (A).

Carol E. Siino
Intellectual Property Coordinator
M.C. 480-106-359
810/986-2520

Attachment

C: Materials & Processes (430)
Chemical & Environmental Sciences (460)
Aerotek (A)

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CORPORATION

File No.

GP-302579

RECORD OF INVENTION

This Record of Invention must be completed with sufficient detail so that your invention can be understood and evaluated by both your engineering management and by a GM Legal Staff patent attorney. Novelty and competitive significance of your invention will be evaluated based on the information you provide.

Invention Title: Hydrogen Storage Medium

Inventor #1
Name: Gregory P.A. Meisner Citizen of: USA
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Social Security No. [REDACTED] GM Employee: ☒ Yes ☐ No ☒ Salary ☐ Hourly ☐ Contract
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GM Address: 30500 Mound Rd, Warren, MI 48090 Mail Code: 480-106-224 FAX Number: (8)-226-3091
Centrex Number
Non-GM Employer: _____ Phone No. _____
(Area Code) + Number
Non-GM Employer Address: _____
Street City and State Zip Code

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Social Security No. [REDACTED] GM Employee: ☒ Yes ☐ No ☒ Salary ☐ Hourly ☐ Contract
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Centrex Number
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(Area Code) + Number
Non-GM Employer Address: _____
Street City and State Zip Code

* If there are more than two (2) inventors for this invention use the template at the end of this form.

File Number:

GP-302579

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1 of 7

Answer questions 1 - completing all of them to the best of your knowledge.

1. This invention was first thought of on:

2. This invention has been or is expected to be disclosed outside GM on: N/A

3. This invention has been used or is committed to be used in production on: N/A

4. This invention has been offered for sale outside GM on: N/A

5. Was this invention made while working on a Government Contract? ☐ Yes ☒ No

If yes, identify the government Contract No. N/A

6. Identify the product or process in which the invention is incorporated: Hydrogen storage, Fuel Cells

7. List all individuals who can provide information about the making of the invention. This list may include individuals who made the first sketch, description, or tests and individuals who are familiar with the facts relating to the making of the invention.
Gregory P. Meisner, Frederick E. Pinkerton, Martin S. Meyer, Michael P. Balogh, Matthew D. Kundrat, Jan F. Herbst, Stephen J. Swarin, and Gary G. Tibbetts.

8. Each inventor has a legal duty to disclose all information known that is material to patentability of this invention. Such information includes the relevant prior art, which may be in the form of current or past products, equipment, processes, materials, patents, publications, advertisements, displays, and unpublished developments and proposals—whether originated by you, others in GM, competitors, suppliers, customers or others. Such information also includes disclosure of this invention outside GM, sales and offers of products using this invention, use of this invention in production and disputes about who should be considered as an inventor of this invention. To comply with the duty to disclose, list here and attach a copy of all such information, to the extent known.

1. Robert Juza and Karl Opp, *Z. anorg. Allg.*, 266, 313 (1951).

2. Phin Chen, "Hydrogen Storage in Metal Nitride Systems", *MRS Spring Meeting*, V5.18 (2002).

Answer question 9 thoroughly.

9. Describe the invention in sufficient detail so that its nature, operation and usefulness can be understood. (Attach drawings, diagrams and further description, when necessary. Additional guidelines are listed below.) This hydrogen storage medium is based upon the following general reversible chemical reaction:

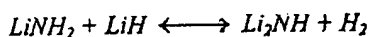


where M is a metal or mixtures of metals (e.g. Li, Na, Mg, Ca, Al, Ti, Fe, Zn, etc.), x is the valence state of the metal or average valence state of the metal mixture, N is nitrogen, and H is hydrogen. The essential material is either the metal imide $[2M^{x+}(NH)_{x/2}]$ or mixture of the metal amide and metal hydride $[M^{x+}(NH_2)_x + M^{x+}H_x]$. The absorption or desorption of hydrogen is determined/controlled by the temperature and hydrogen pressure of the storage medium.

We have demonstrated this hydrogen storage medium in the lithium system: $Li_2NH + H_2 \longleftrightarrow LiNH_2 + LiH$.

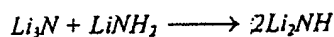
This system can be formed from a wide variety of starting materials and preparation techniques including but not limited to the following:

1. Mixing an equal molar ratio of lithium amide ($LiNH_2$) and lithium hydride (LiH) according to the following reaction.



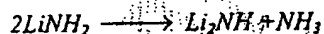
We have demonstrated this method in the laboratory. Mixing was accomplished using standard ball milling techniques.

2. Reacting an equal molar ratio of lithium nitride (Li_3N) and lithium amide ($LiNH_2$) according to the following reaction:



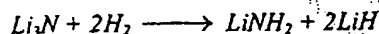
We have demonstrated this method in the laboratory. Mixing was accomplished using standard ball milling techniques.

3. Evolving ammonia from lithium amide ($LiNH_2$) according to the following reaction:



We have demonstrated this method in the laboratory.

4. Hydriding lithium nitride (Li_3N) according to the following reaction:



This method has been demonstrated in the laboratory, but it produces excess lithium hydride which decreases the hydrogen storage capacity of the device.

The lithium system absorbs hydrogen at temperatures of $\geq 145^\circ\text{C}$ and hydrogen pressures of $\geq 5\text{-}15\text{KPa}$ and desorbs at temperatures $\geq 125^\circ\text{C}$ and hydrogen pressures $\leq 10\text{KPa}$.

Mechanical and Electrical Devices: Include illustrations assigning reference numbers to the main elements and refer to the reference numbers in a description that explains how the main elements are connected or related and how they operate.

Electrical Circuits and Controls: Include circuit diagrams and a functional description.

Computer Software and Manufacturing or Business Processes: Include a flowchart or other step-by step overview.

Chemical Inventions: Identify all essential materials used, and alternatives therefor, in chemical terms – not tradenames. Identify and quantify all significant variables (e.g. temperature, pressure, concentration, pH etc.) of the process or material specifying operating ranges and the preferred example. Discuss the significance of each variable. Provide a recipe for at least one working example of the invention.

I hereby assign this invention to General Motors Corporation
and authorize General Motors Corporation to file an application on my behalf.

Gregory P. Melsner
INVENTOR - SIGNATURE

GREGORY P. MELSNER
(ALSO, PRINT NAME)

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Frederick E. Pinkerton
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Frederick E. Pinkerton
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Martin S. Meyer
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Michael P. Balogh
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Matthew D. Kundrat
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This invention was reviewed and understood by me:

Stephen J. Swarin
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Stephen J. Swarin
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DATE

Jan F. Herbst
2nd WITNESS - SIGNATURE

Jan F. Herbst
(ALSO, PRINT NAME)

DATE

Answer the following questions if helpful in describing this Invention

10. What benefits will be realized by using this invention?

The benefit of this invention is a feasible hydrogen storage medium for automotive applications.

11. What is the state of development of this invention?

Reversible hydrogen storage has been successfully demonstrated in the lithium imide (Li_2NH), lithium amide (LiNH_2), and lithium hydride (LiH) system.

12. To the extent known, what alternatives exist for accomplishing substantially the same result as this invention?

Hydrogen can be stored either as a compressed gas, cryogenically cooled liquid, or in a solid. Solid hydrogen storage includes high surface area carbonaceous material, or hydrogen containing materials (e.g. MgH_2 , Mg_2NiH_4 , LaNi_5H_6 , NaAlH_4 , NaBH_4 , LiBH_4 , etc.). Current hydrogen storage systems lack capacity, have slow kinetics, have poor shelf life, require high or low temperatures, require high pressures, or are not reversible. Thus, they are not practical for automotive applications.

13. Describe the background of the invention. This description may include the state of the prior art and may identify deficiencies in the prior art that are overcome by this invention.

At the 2002 Materials Research Society (MRS) Spring Meeting, Ping Chen of the National University of Singapore presented her work on "HYDROGEN STORAGE IN METAL NITRIDE SYSTEMS". In this presentation, Ping Chen presented her work showing Lithium nitride (Li_3N) absorbs hydrogen forming lithium amide (LiNH_2) and lithium hydride (LiH), claiming that the reaction is reversible. Our work shows that the reaction is not reversible, but in fact desorbs hydrogen to form lithium imide (Li_2NH). Our work also shows that starting from lithium nitride results in excess lithium hydride, which does not contribute to reversible hydrogen storage. Therefore we have identified new synthesis routes that eliminate the excess lithium hydride.

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File Number: GP 302579

Inventor # 5

Name: Matthew D. Kundrat Citizen of: USA
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File Number: 6F 302579

Hydrogen Storage Medium

GP-302579

Greg Meisner, Fred Pinkerton, Martin Meyer, Mike Balogh,

Matt Kundrat

What is the Idea?

- Reversibly store H_2 using a metal imide
- The H_2 is released by heating the storage medium
- Four synthesis routes identified

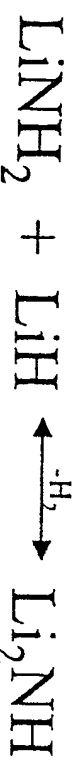
Li-N-H Reactions



Reversible H₂ storage capacity 5.2 wt%



Reversible H₂ storage capacity 6.5 wt%



Reversible H₂ storage capacity 6.5 wt%



Reversible H₂ storage capacity 6.5 wt%

(ROI: Meisner, Pinkerton, Meyer, Balogh, & Kundrat)

How does it work?

- H₂ reacts with the imide forming the hydride & amide:



where M is Li, Na, Mg, etc... and x is the valence state.

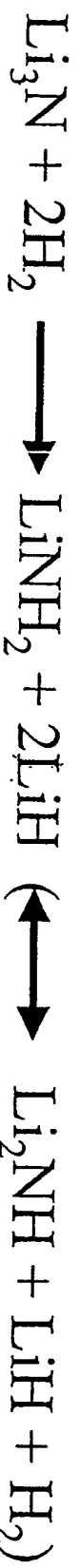
- Heating releases the H₂ and reforms the imide.
- H₂ storage demonstrated in the lithium system:



(6.5wt% theoretical reversible capacity)

Prior art

- H₂ storage in lithium nitride previously reported*.



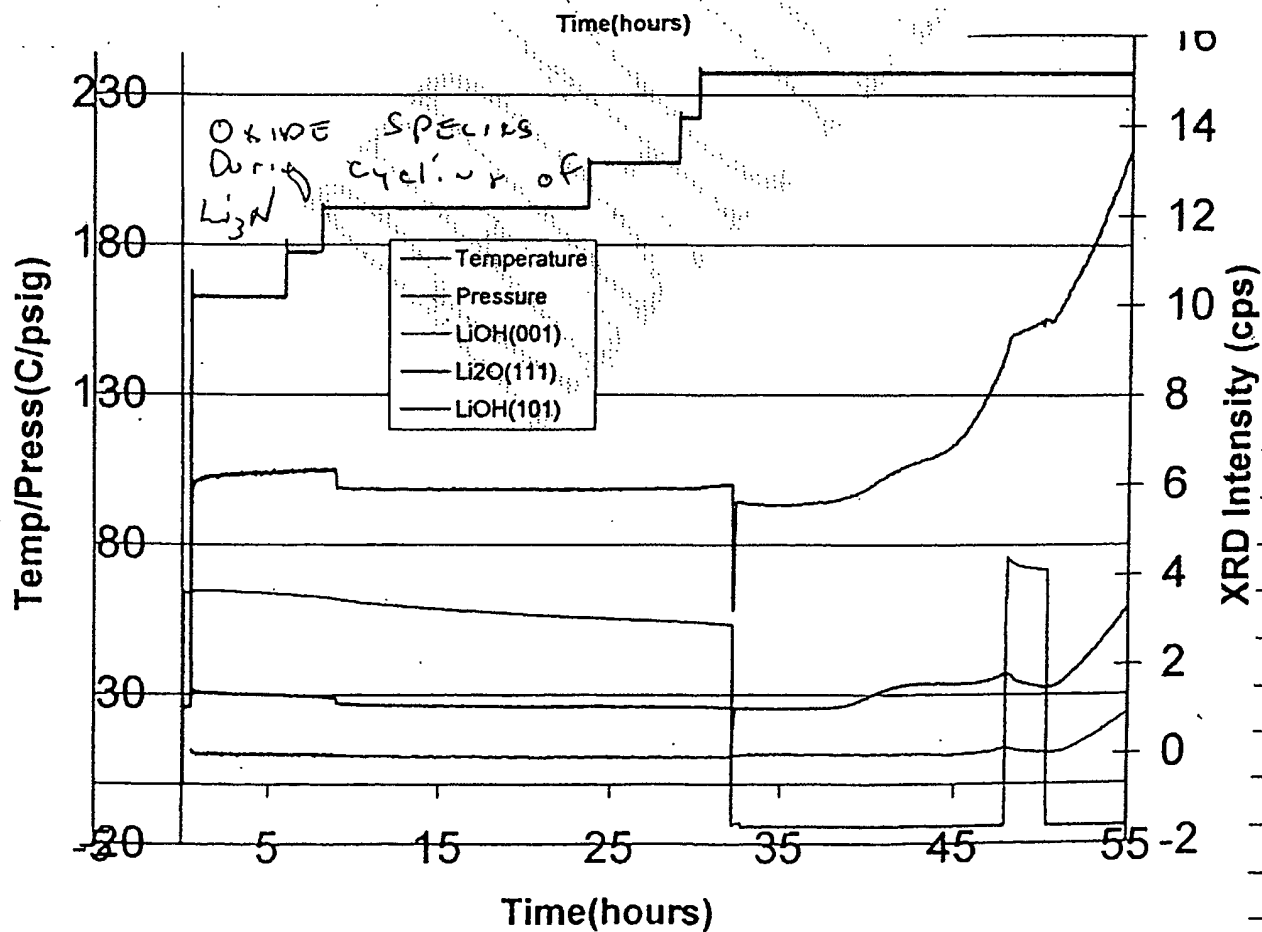
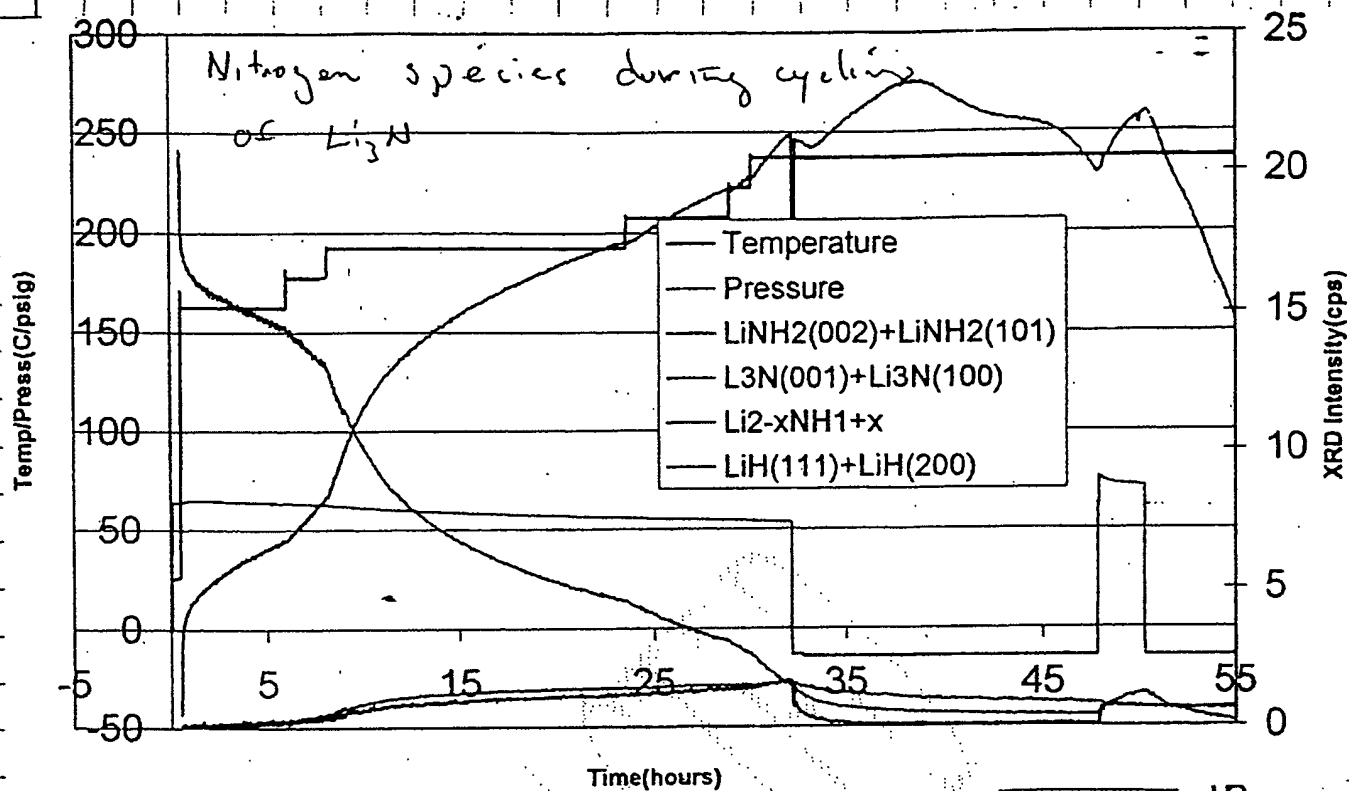
(5.2wt% theoretical reversible capacity)

**Ping Chen, Materials Research Society Symposium Proceedings, v 730, V5.18, April 2002*

EXHIBIT B

37 C.F.R. §1.131 Declaration of Gregory P. Meisner
U.S.S.N. 10/824,876 entitled "Imide/Amide Hydrogen Storage Materials and Methods."

DATE



WITNESSED

Jeffrey E. Puntieri

WITNESSED

David Swan

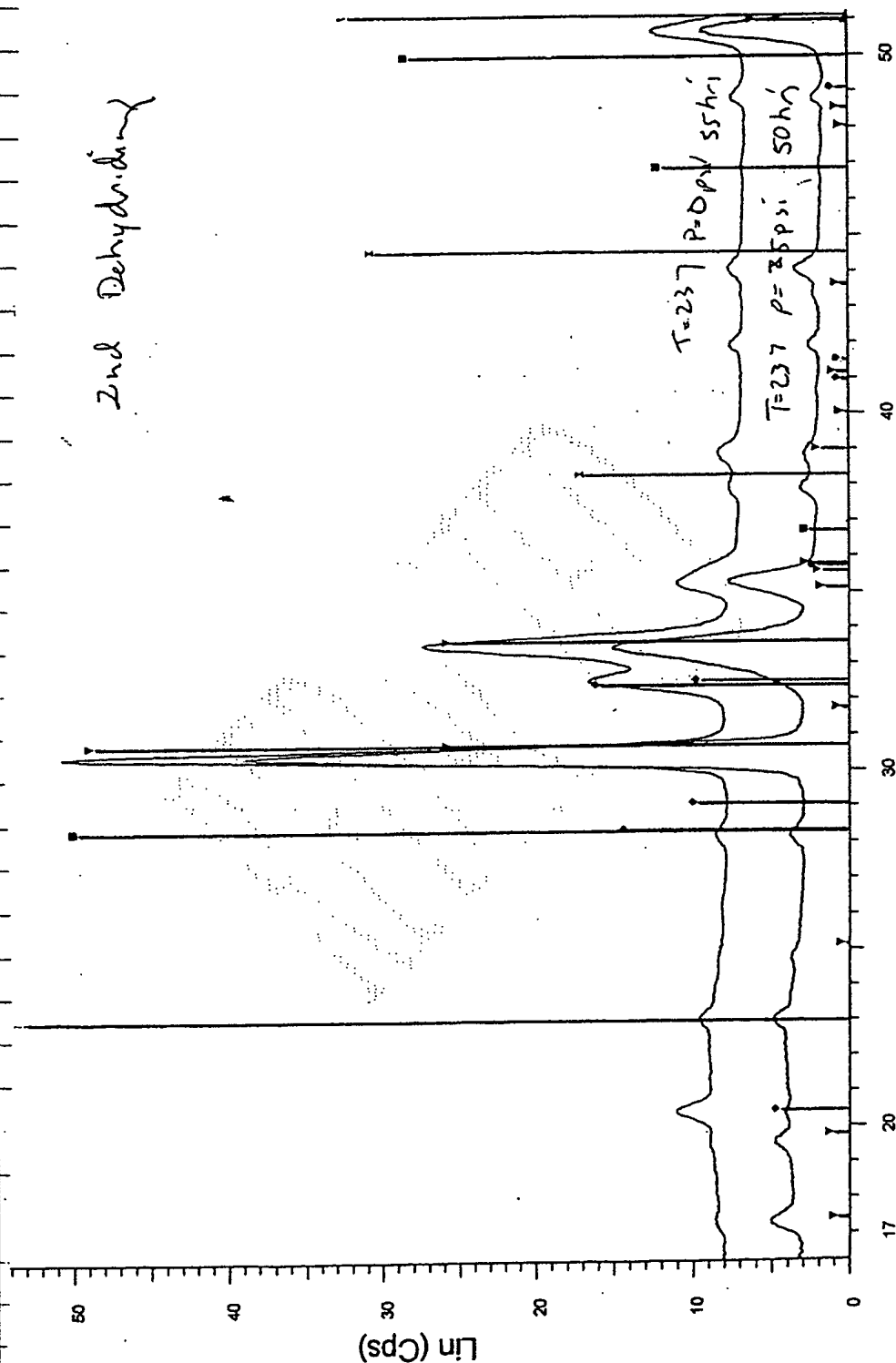
SIGNATURE

Michael P. B...

94

DATE

2nd Dehydrodimer



2-Theta - Scale

- ☒ test [027] - File: p783c_04a [027].RAW - Type: 2Th alone - Start: 1
☒ test [082] - File: p783c_04a [082].RAW - Type: 2Th alone - Start: 1
☒ 32-0564 (*) - Lithium Hydroxide - LiOH - Y: 18.20 % - d x by: 1. - WL: 1
☒ 76-0821 (C) - Lithium Nitride - Li3N - Y: 115.05 % - d x by: 1. - WL: 1
☒ 78-2005 (C) - Lithium Nitride - Li3N - Y: 40.57 % - d x by: 1. - WL: 1
☒ 75-0050 (C) - Lithium Imide - Li2NH - Y: 95.67 % - d x by: 1. - WL: 1
☒ 75-0049 (C) - Lithium Amide - LiNH2 - Y: 50.00 % - d x by: 1. - WL: 1
☒ 09-0189 (N) - Lithium Hydride - LiH - Y: 59.71 % - d x by: 1. - WL: 1
☒ 77-2144 (C) - Lithium Oxide - Li2O - Y: 50.00 % - d x by: 1. - WL: 1

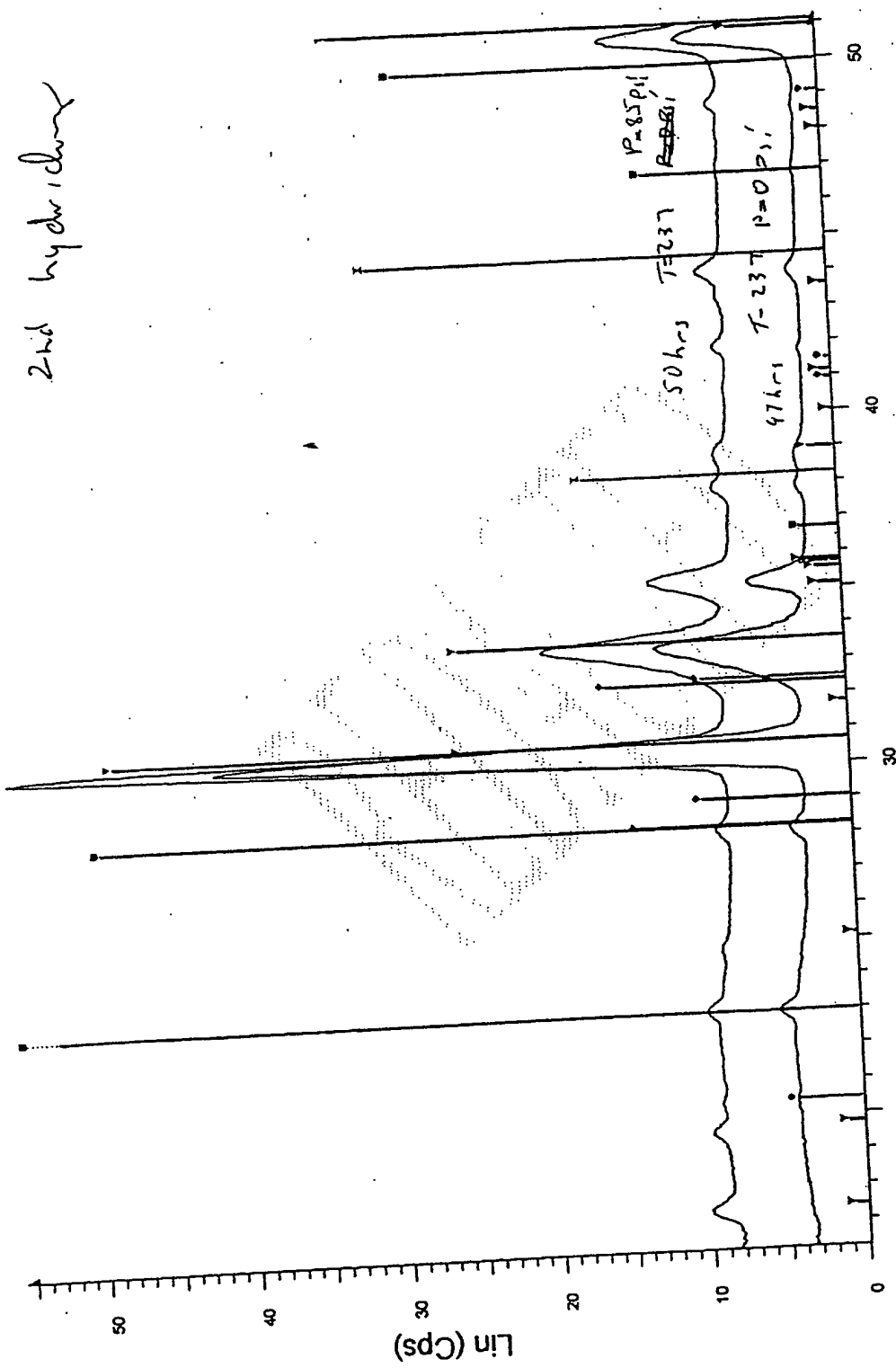
WITNESSED

WITNESSED

SIGNATURE

TE

2nd hydrolysis



2-Theta - Scale

- test [172] - File: p783o_03 [172].RAW - Type: 2Th alone - Start: 16
- test [027] - File: p783c_04a [027].RAW - Type: 2Th alone - Start: 1
- 32-0564 (*) - Lithium Hydroxide - LJOH - Y: 16.57 % - d x by: 1. - W
- 76-0821 (C) - Lithium Nitride - L3N - Y: 104.73 % - d x by: 1. - WL:
- 76-2005 (C) - Lithium Nitride - L3N - Y: 36.93 % - d x by: 1. - WL: 1

WITNESSED

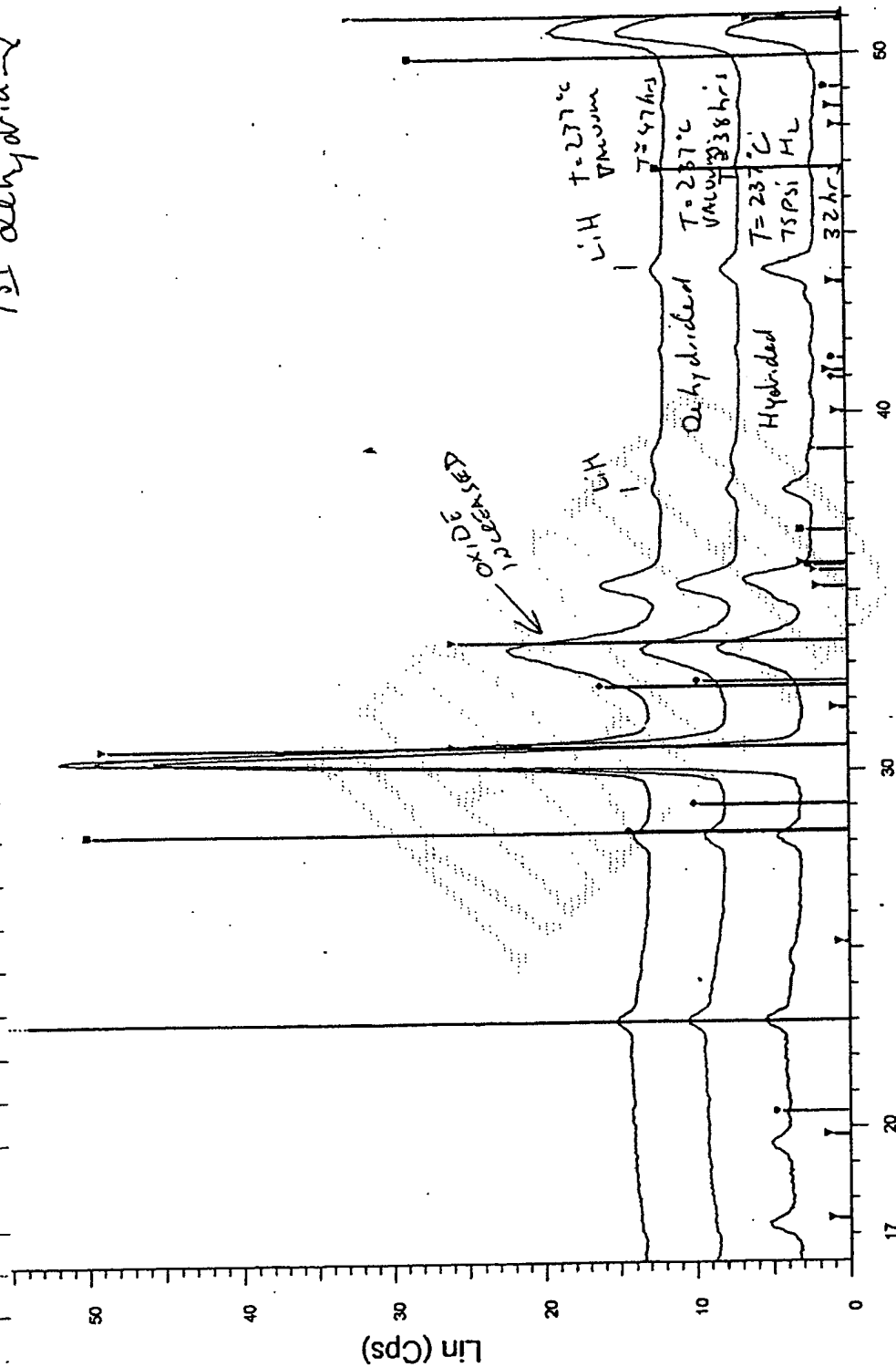
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[Signature]

SIGNATURE

1st dehydride

thru



2-Theta - Scale

- ☒ test [455] - File: p783c_02 [455].RAW - Type: 2Th alone - Start: 16. ☒ 76-2005 (C) - Lithium Nitride - Li3N - Y: 39.73 % - d x by: 1. - WL: 1
- ☒ test [085] - File: p783c_03 [085].RAW - Type: 2Th alone - Start: 16. ☒ 75-0050 (C) - Lithium Imide - Li2NH - Y: 93.68 % - d x by: 1. - WL: 1
- ☒ test [172] - File: p783c_03 [172].RAW - Type: 2Th alone - Start: 16. ☒ 75-0049 (C) - Lithium Amide - LiNH2 - Y: 48.96 % - d x by: 1. - WL: 1
- ☒ 32-0564 (*) - Lithium Hydroxide - LiOH - Y: 17.82 % - d x by: 1. - W
- ☒ 76-0821 (C) - Lithium Nitride - Li3N - Y: 112.66 % - d x by: 1. - WL: 1

WITNESSED

[Signature]

WITNESSED

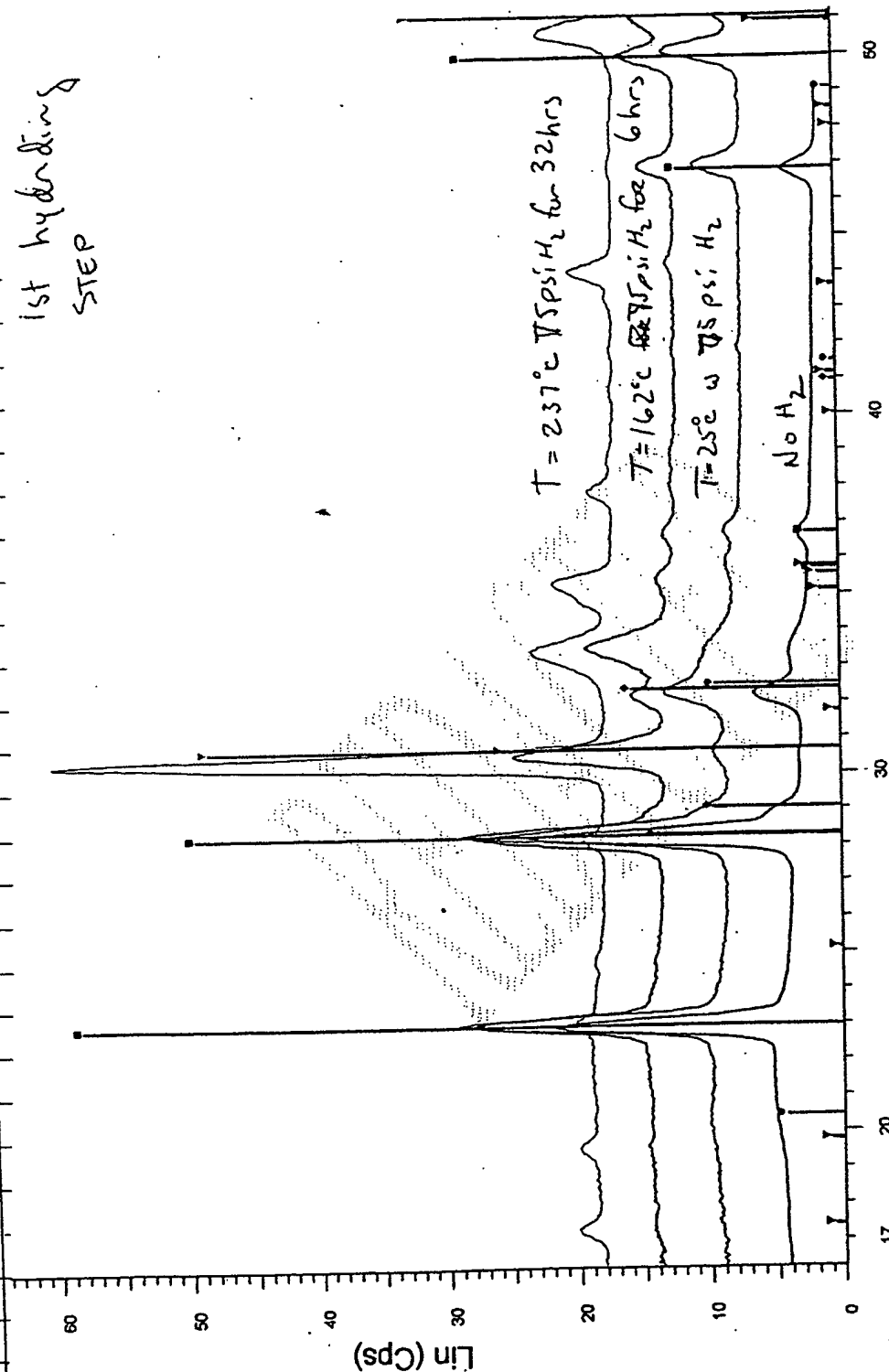
[Signature]

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[Signature]

DATE

1st hydrating
STEP



2-Theta - Scale

- 78-0821 (C) - Lithium Nitride - L13N - Y: 96.34 % - d x by: 1. - WL: 1
- 78-2005 (C) - Lithium Nitride - L13N - Y: 33.97 % - d x by: 1. - WL: 1
- 75-0050 (C) - Lithium Imide - L12NH - Y: 80.11 % - d x by: 1. - WL: 1
- 75-0049 (C) - Lithium Amide - L1NH2 - Y: 41.87 % - d x by: 1. - WL: 1
- 783(pentane) [002] - File: p783(pentane)_01 [002].raw - Type: 2Th
- test [001] - File: p783c_01a [001].RAW - Type: 2Th alone - Start: 1
- test [308] - File: p783c_01a [308].RAW - Type: 2Th alone - Start: 1
- test [455] - File: p783c_02 [455].RAW - Type: 2Th alone - Start: 16
- 32-0564 (*) - Lithium Hydroxide - L1OH - Y: 15.24 % - d x by: 1. - W

WITNESSED *Frederick L. Ricketts*

WITNESSED *John J. Swan*

SIGNATURE *Michael B. [Signature]*

90

DATE

[REDACTED] thru [REDACTED]

Li₃N Hydrogen Storage Rxn

In situ XRD Li₃N obtained from
 E. Pinkerton washed w Pentane
 XRD Files p783e-01 000.gfrm -

" -01-475

" -07 000.gfrm -

-02-454

03-000

03-183

04-000

04-082

Dany lab Cites =

~~Emp D~~

MAN-013 ASC -en

MAN-014 ASC

15 ASC

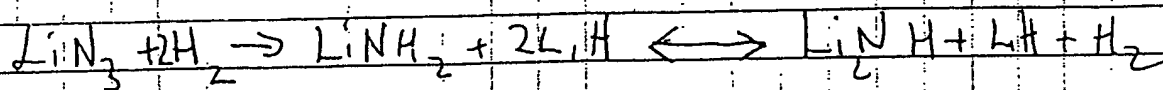
16 ASC

17 ASC

18 ASC

Reaction from XRD Phase

~~Results~~
 analysis



WITNESSED

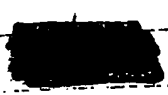
Fredrick E. Pinkerton [REDACTED]

WITNESSED

[REDACTED]

SIGNATURE

Michael P. B. [REDACTED]



$P_m = 153.7$

$T_s = 21.2$

end log file

$T_m = 26.9$

$T_F = 22.0^\circ C$

Li_3N powder loaded

log file Li_3N_001 log 20 sec

Li_3N	9.955 (holder)
	10.700 siph + holder
	$\Rightarrow 0.745$ g
	+ wash ~ 45 mg

heat to $150^\circ C$ valves S, L, F open $T_{sp} = 170$

at 9:59am # 568

$T_s = 153.7$

$T_F = 156$

$T_{sp} = 170$

Run PCI : Small Holder # 25

Li_3N

Li_3N 1st Run $156^\circ C$

about

* 100 slm

300 sec

1.79 g/cc

8000. mmHg

0.745 gms

High Res

ρ : estimated from

$LiNH_2$ $r = 1.178$

$$\rho_{Li_3N} \approx (1.178) \frac{34.83 \text{ g/mole } Li_3N}{22.96 \text{ g/mole } LiH_2N}$$

$$= 1.79 \text{ g/cc}$$

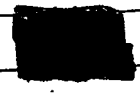
$T_{sp} = 170^\circ C$

$T_F = 157^\circ C$

$T_s = 154.9^\circ C$



Run end @ 22:25



$x = 7.51$ 56.42 mg $T = 159.0^\circ C$

not much description

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